EEC CHINA PROJECT NA 85/27

STUDY OF RUBBER SAMPLES FROM DIFFERENT FACTORIES ON HAINAN ISLAND

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I. INTRODUCTION

Following the visit by Messrs. Laigneau and Sainte Beuve to different factories on Hainan Island in November 1991, and the comments made by Chinese rubber consumers about 100% modulus weakness, rubber samples were taken at random and analyzed in our laboratories in France.

II. PROCESSING PROCEDURES

II.1. XIN ZHONG

The hevea plantation covers around 5,300 ha, 4,000 ha of which are currently being tapped. Production amounts to approximately 4,000 tonnes of dry rubber per year.

*** Clones**

The plantation is mostly made up of old seedlings and PR107. The trees vary considerably in age; the oldest plantings date from 1960 and planting was staggered up to 1980. Today, the concession is entirely planted and the old seedlings are being replaced by budded planting material.

*** Tapping system**

Tapping begins in April and ends in December. The trees are tapped in S4, D/3, i.e. 80 tappings per year. Stimulation is carried out twice a month, or only once if the relative humidity is low.

Average production at the plantation would seem to be around 1 t/ha/year; however, it should be pointed out that the trees are grown on terraces. Despite all this, planting density would appear to be around 560 trees/ha.

II.1.2. Latex line

Latex is delivered to the factory preserved at a rate of O.05% NH3 and is filtered to remove impurities (>40 mesh).

It is diluted to 23% in homogenization tanks, then acidified with acetic acid in a matched flow system at a rate of 11 g of neat acid per dry kg in the form of a 2% diluted solution; it is then poured into aluminium troughs into which a sodium bisulphite solution is sprayed. After maturing for 12 hours, the coagulum goes to the crusher, then through three crepers in series and a creper-hammermill. The crumbs are dried in 6 two-tier trolleys containing 500 kg of dry rubber for 4 hours at 115/120°C.

The 40 kg bales are pressed for a maximum of 60 seconds at 100 tonnes, then double wrapped in a polyethylene bag and a woven polypropylene bag. The colour of the rubber is that of a good 5L, but there are a few black spots, probably caused by the dryer.

II.1.2. Secondary grade line

Cup lumps and tree scrap are soaked in the same tank for 2 to 3 days before processing. The line comprises a washer and two crepers with a diameter of 200 mm and different grooving through which the rubber is passed 2 x 6 times. The resulting crepes then go to the latex line after the crusher. The single layer of crumbs is placed in the dryers and dried at 100/115°C for 4 hours. The rubber is then unmoulded and pressed without prior cooling. Wrapped bales are stored in bulk in the storeroom.

II.1.3. Quality of the rubber produced

The production at this plantation is 90% 5L, i.e. 3,000 tonnes. This situation would seem to be due to a combination of two factors linked to climate: relatively short flow period (stops around 1:00 pm) and good latex stability in the cup.

II.2. XI QING

The rubber plantation covers 4,900 ha, 3,100 ha of which are currently being tapped.

*** Clones**

The plantation is made up of old seedlings (60%) and young budded material, mainly PR107.

*** Tapping system**

Tapping begins in mid-April and ends in mid-December. The trees are tapped in S2, D/2, i.e. 120 tappings per year. Stimulation is carried out twelve times per year with an ethylene generating product at 2% active ingredient.

Average production at the plantation would appear to be around 730 kg/ha/year and planting density seems to be around 560 trees per hectare.

II.2.1. Latex line

Latex is delivered to the factory preserved at a rate of 0.04% NH3 and is filtered by clarification to remove impurities and precoagula.

It is diluted to 22% in two homogenization tanks, then acidified with acetic acid in a matched flow system at a rate of 10 g of acid per dry kg in a 3/4% solution. It is then poured into very long (75 m) aluminium troughs into which a sodium bisulphite solution is sprayed. The crumbs are dried for 4 hours at 115°C for grade 5 and 3½ hours at 110°C for grade 10. The trolleys are loaded with very thick layers of crumbs. There are 4 PVC chimneys at the bottom of the trolleys to provide a directed air flow; the crumb cakes are over 50 cm high at the end of drying. They are cut in two lengthwise before being pressed for a minute at 150 tonnes to form 40 kg bales, then double wrapped in a polyethylene bag and a woven polypropylene bag.

II.2.2. Secondary grade line

Cup lumps and tree scrap are mixed together in a tank of water and are soaked for 7 days; they then go to a washer and 3 crepers, and then to the latex line.

II.2.3. Quality of the rubber produced

Production at this plantation is 92% 5L, i.e. 2,082 tonnes. This situation appears to stem from a combination of two climatic factors: temperature and humidity.

II.3. DONG PING

The hevea plantation covers 3,730 ha, 1,240 ha of which are currently being tapped.

*** Clones**

The plantation is made up of young trees, mainly PR 107, RRIM 600 and PB 86. All the plantings prior to 1976 have been rejuvenated with budded material and there are no longer any seedlings.

*** Tapping system**

Tapping starts at the beginning of April and finishes at the end of December. The trees are tapped in S2, D/2, i.e. 135 tappings per year. Stimulation is carried out twice a month, or only once when the relative humidity is low. The stimulant used is a simple aqueous solution containing 2% ethylene gas; Ethrel seems to be unheard of on the State farms.

Average production at the plantation appears to be around 1,600 kg/ha/year and planting density around 560 trees per hectare.

II.3.1. Latex line

Latex is delivered to the factory preserved at a rate of 0.03 to 0.05% NH_3 and is filtered to remove impurities (>40 mesh). It is diluted to 23% in 2 homogenization tanks, then acidified with acetic acid in a matched flow system at a rate of 6 g of acid per dry kg in the form of a 2% diluted solution. It is then poured into aluminium troughs into which a sodium bisulphite solution is sprayed; after maturing for 12 hours, the coagulum goes to a crusher, then through 3 crepers in series and a creper-hammermill. The crumbs are dried for 4 hours at 110°C in 6 two-tier trolleys containing 500 kg of dry rubber. The 40 kg bales are pressed for a maximum of 15 seconds at 100 tonnes, then double wrapped in a polyethylene bag and a woven polypropylene bag. The colour of the rubber is that of a good 5L, though there are a few black spots.

II.3.2. Secondary grade line

Cup lumps and tree scrap are soaked in the same tank for 1 to 2 days before processing. The line includes a washer and 2 crepers with a diameter of 200 mm and different grooving depths, through which the rubber is fed 2 x 6 times. The resulting crepes then go to the latex line after the crusher. The crumbs are laid in a single layer in the dryers and dried for 4 hours at 105°C. The rubber is then unmoulded and pressed without prior cooling. Wrapped bales are stored in bulk in the storeroom.

II.3.3. Quality of the rubber produced

The production at this plantation is 91% 5L, i.e. 1,843 tonnes. This situation appears to stem from a combination of 2 climatic factors: temperature and humidity. In the Summer, the trees are tapped at 3:00 am and collection takes place at 9:00 am, by which time the flow has already stopped. In the Winter, the trees are tapped at 6:00 am and collection takes place at 11:00 am and at 4:00 pm if necessary, when the latex has already stopped flowing.

Characteristics	XIN ZHONG	XI QING	DONG PING
Clones	Old seedlings PR 107	Old seedlings (60%) PR 107 (young)	PR 107/RRIM 600 PB 86 young trees
Tapping system	S4/D3	S2/D2	S2/D2
Stimulation	Twice a month	12 times/year with 2% ethylene generator	Twice a month with 2% ethylene generator
Preservation, NH3 (%)	0.05	0.04	0.04
Dilution (%)	23	22	23
Acidification (g per kg of dry rubber)	11	10	6
Maturation (hrs)	12	-	12
Sodium bisulphite spraying	Yes	Yes	Yes
Crumbing	Malaysian type	Malaysian type	Malaysian type
Drying Duration (hrs) Temperature (°C)	 4 115/120	 4 115	 4 110
Pressing (t) Duration (sec)	100 60	150 60	100 15

III - SAMPLE ANALYSIS

III.1. RAW RUBBER PROPERTIES

The following measurements were taken after homogenization in accordance with ISO 2000 (10 passes at 70° C):

- Mooney viscosity ML(1+4) at 100° C
- Wallace plasticity Po and PRI
- Gel rate measurement
- Performance on elasticity meter

The analysis results are given in the following table

Reference	ML(1+4) 100°C °M	Wallace Plasticity		Gel rate	
		Po*	PRI	Individual values %	Mean %
Xin Zhong 15-11	85	41	82	8.13 8.53 8.28	8.31
Xi Qing 5-11	85	47.5	78	12.31 10.44 12.90	11.88
Dong Ping 16-11	80	37	74	15.27 15.60 14.20	15.02
Dong Ping 14-10-91	74.5	39.5	81	9.56 10.33 10.08	10.12

* Wallace Plasticity was measured in accordance with ISO 2007, using Job 38a paper (14 g/m^2)

The results vary somewhat between the different factories, which is quite surprising since clones and the process are virtually identical for the first two; there is a tree age effect at the Dong Ping factory.

III.2. ASSESSMENT IN ACS1 BLEND

The blends were made up using the following procedure based on standard NFT 43.001.

Formula:

Homogenized rubber	190 g
Master-blend A	12.5 g
Master-blend S	18.5 g

The mixer rollers were heated to 70°C and the gap between the guides was reduced to 24 cm. The space between the rollers was around 0.5 mm.

a) Form the rubber sleeve around the front roller; finely adjust the gap between the rollers so as to obtain a rolling bank of rubber around 15 to 20 mm in diameter.

b) Add master-blend A in one go; cut the blend entirely twice (at 15 sec and 35 sec), roll it and re-introduce it perpendicularly.

c) Do likewise, adding master-blend S.

d) Take the blend and homogenize it by passing it 6 times at 0.8 mm, rolling it and introducing it perpendicularly.

e) Stretch the blend into 2 mm sheet.

III.2.1. Properties of raw mixtures

Vulcanization kinetics were carried out on the Monsanto rheometer at 160°C with a 3° oscillation arc.

The rheograms can be found in the annex.

Reference	ML1+4 100°C(°M)	ML (N.m)	M HR (N.m)	ts (0.2)(min)	t'c 90 (min)
Xin Zhong 15/11	46	1.58	5.20	1.42	10.5
Xi Qing 5/11	50	1.67	5.31	1.67	9.5
Dong Ping 16/11	46	1.58	5.09	1.58	9.75
Dong Ping 14/10	46	1.55	5.03	1.75	10.5

In ACS1 blend, the differences between factories are levelled out but remain significant.

III.2.2. Mesurement of 100% modulus - ISO 37 - 1977

The 100% stretching modulus values were determined on two types of test-piece, H1 and H2, with a Lo of 20 and 10 mm respectively after vulcanization for 40 min at 140°C.

The values given in the following table reveal good similarity between the two types of test-piece.

Reference	Test-piece H1		Test-piece H2	
	100% Modulus (MPa)	Corrected 100 Mod (MPa)	100% Mod. (MPa)	Corrected Mod 100
Xin Zhong 15/11	0.71	0.69	0.70	0.68
Xi Qing 5/11	0.71	0.68	0.70	0.67
Dong Ping 16/11	0.70	0.68	0.70	0.68
Dong Ping 14/10	0.66	0.65	0.67	0.66

Apart from the production at the Dong Ping factory on 14th October, the other results were very consistent.

III.3. STUDY OF VISCO-ELASTIC CHARACTERISTICS MEASURED ON THE ELASTICITY METER

III.3.1. Experimental procedure

In all the trials, the elasticity meter parameters were those usually applied, i.e.:

- sample temperature 70°C
- maximum deformation rate 60%
- deformation speed 1, 3, 10, 30 and 100% deformation per second
- type of stress linear deformation, the measurement of recovery
- recovery recording after 25 min
- measurements carried out on homogenized rubber

The following parameters were calculated:

* for viscosity : n, K and K100
n and K are power law constants

$a = Kv^{-n}$ or $a = F/v$

F being the force value at the end of deformation
v the stress speed

K100 is bulk viscosity for a speed of 100% deformation/sec

* for elasticity : R(0.1/1), R(0.1/100), R(10/1), R(10/100)

R (X/Y) is the recovery measured after a time equal to X times the deformation time for stress exerted at a rate of $Y\%.s^{-1}$. The elastic recovery R(t) is defined as being the increase in test-piece height compared to the variation in height of the test piece under stress. R(0.1/1) and R(0.1/100) are used to assess initial recovery and R(10/1) and R(10/100) to obtain a value similar to a state of equilibrium, for extreme stress rate values: 1 and $100\%.s^{-1}$.

The precision of the results is 5% for the viscosity parameters and 2% for the elasticity parameters.

III.3.2. Results

Reference	n	k(N,S)	k100	R(O.1/1)	R(10/1)	R(0.1/100)	R(CO/100)
Xin Zhong 15/11	0.800	8709	219	0.450	0.821	0.669	0.940
Xi Qing 5/11	0.819	10172	234	0.496	0.856	0.717	0.964
Dong Ping 16/11	0.808	8616	209	0.472	0.836	0.654	0.952
Dong Ping 14/10	0.775	7151	201	0.418	0.821	0.634	0.938

The elastic recovery curves are given in the annex.

For the two rubbers with the same Mooney viscocity, Xin Zhong and Xi Qing (cm = 85), the parameters from the elasticity meter were substantially different, particularly for the viscosity parmeter K and for the elastic recovery parameters.

The recovery values measured after 0.1 times the deformation time show the greatest differences.

IV - CONCLUSION

The analyses carried out in this initial investigation on 4 rubber samples reveal a certain dispersed tendency. Contrary to the view of manufacturers, we did not find any very low 100% modulus values. It was at an average value for each of the four samples and corresponds to rubber made from ICR type field latex.

All this requires confirmation. A more extensive study needs to be made, involving 2 or 3 representative factories and analyses carried out throughout an entire season.

Finally, Mr. Piton's mission, which was initially planned for correcting and improving modulus values by modifying the process no longer seems necessary.

While remaining to be confirmed, the problem would seem to be too great a dispersion of the results of analyses carried out on raw rubber and involving physical properties (plasticity, maximum torque, etc.).

I.R.A.P.
GB/ML

5 mai 1992

ETUDE DE 4 CAOUTCHOUCS CHINOIS PROVENANT DE DIFFERENTES USINES SITUEES DANS L'ILE de HAINAN

Commande CT TECHNO 389/91 du 28/11/91

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1 - PROPRIETES DES CAOUTCHOUCS CRUS

Les mesures suivantes ont été réalisées après homogénéisation ISO 2000 des échantillons:

- Consistance Mooney ML 1+4 à 100°C.
- Plasticité Wallace Po et PRI.
- Mesure du taux de gel.
- Comportement à l'élasticimètre (voir paragraphe 3).

Référence	ML (1+4) 100°C °M	Plasticité Wallace PO	PRI	Taux de Gel Valeurs Individuelles %	Moy. %
XIN Z HONG	85	41	82	8,13 8,53 8,28	8,31
XI YING	85	47,5	78	12,31 10,44 12,90	11,88
DONG-PING 16/11	80	37	74	15,27 15,60 14,20	15,02
DONG-PING 5L 22/11	74,5	39,5	81	9,56 10,33 10,08	10,12

2 - EVALUATION EN MELANGE ACS 1

Les mélanges ont été effectués conformément au mode

opératoire utilisé pour les essais interlaboratoires.

2.1 - Propriétés des mélanges crus

Les cinétiques de vulcanisation ont été réalisées au rhéomètre Monsanto à 160°C avec un arc de 3° d'oscillation.

Les rhéogrammes sont joints en annexe.

Référence	ML 1+4 100°C (oM)	ML (N.m)	M HR (N.m)	ts (0,2) (min)	t'c 90 (min)
XIN Z HONG	46	1,58	5,20	1,42	10,5
XI VING	50	1,67	5,31	1,67	9,5
DONG-PING 16/11	46	1,58	5,09	1,58	9,75
DONG-PING 5L 22/11	46	1,55	5,03	1,75	10,5

2.2 - Mesure du Module 100%

Les modules à 100% d'allongement ont été déterminés sur les 2 types d'éprouvettes H1 et H2 avec respectivement un Lo de 20 et 10 mn après une vulcanisation de 40 min à 140 °C.

Les valeurs consignées dans le tableau ci-dessous montrent une bonne similitude entre les 2 types d'éprouvette.

Référence	Eprouvette H1		Eprouvette H2	
	Mod 100% (MPa)	Mod100 Corrigé (MPa)	Mod 100% (MPa)	Mod100 Corrigé
XIN Z HONG	0,71	0,69	0,70	0,68
XI VING	0,71	0,68	0,70	0,67
DONG PING I6/11	0,70	0,68	0,70	0,68
DONG PING 5L 22/11	0,66	0,65	0,67	0,66

3 - ETUDE DES CARACTERISTIQUES VISCOELASTIQUES MESUREES A L'ELASTICIMETRE

3.1 - Procédure expérimentale

Pour tous les essais, le paramétrage de l'élasticimètre est celui appliqué habituellement, à savoir:

- température de l'échantillon.... 70°C
- taux de déformation maximum..... 60%
- vitesse de mise en déformation.. 1, 3, 10, 30 et 100% de déformation par seconde
- type de sollicitation..... déformation linéaire, puis mesure de la reprise
- enregistrement de la reprise pendant 25 min
- mesures effectuées sur des gommes homogénéisées

Les paramètres calculés sont les suivants:

* pour la viscosité: n, K et K100
  n et K sont les constantes de la loi puissance

  $\eta_a = Kv^{-n}$ où $\eta_a = F/v$

  F étant la valeur de la force en fin de déformation
  v la vitesse de sollicitation

  K100 est la viscosité apparente pour une vitesse de 100% de déformation par seconde.

* pour l'élasticité: R(0,1/1), R(0,1/100), R(10/1) et R(10/100)

  R(X/Y) est la reprise mesurée après un temps égal à X fois le temps de déformation pour une sollicitation effectuée à une vitesse de $Y\%.s^{-1}$. La reprise élastique R(t) est définie comme l'augmentation de hauteur de l'éprouvette rapportée à la variation de hauteur de l'échantillon au cours de la sollicitation. R(0,1/1) et R(0,1/100) permettent d'apprécier la reprise dans ses premiers instants et R(10/1) et R(10/100) d'obtenir une valeur proche d'un état d'équilibre, pour des valeurs extrêmes de la vitesse de sollicitation: 1 et $100\%.s^{-1}$.

La précision des résultats est pour les paramètres de viscosité de 5% et pour les paramètres d'élasticité de 2%.

3.2 - Résultats

Référence	n	k (N,S)	k100	R(0,1/1)	R(10/1)	R(0,1/100)	R(CO/100)
XIN Z HONG	0,800	8709	219	0,450	0,821	0,669	0,940
XI VING	0,819	10172	234	0,496	0,856	0,717	0,964
DONG PING 16/11	0,808	8616	209	0,472	0,836	0,654	0,952
DONG PING 5L 22/11	0,775	7151	201	0,418	0,821	0,634	0,938

Les courbes de reprise élastique sont données en annexe.

Pour les deux caoutchoucs de même consistance Mooney XIN Z HONG et XI VING (cm=85), les paramètres issus de l'élasticimètre sont sensiblement différents, notamment pour le paramètre de viscosité K et pour les paramètres de reprise.

Ce sont les reprises mesurées après 0,1 fois le temps de déformation qui présentent les plus grandes différences.

ANNEX

Rheograms

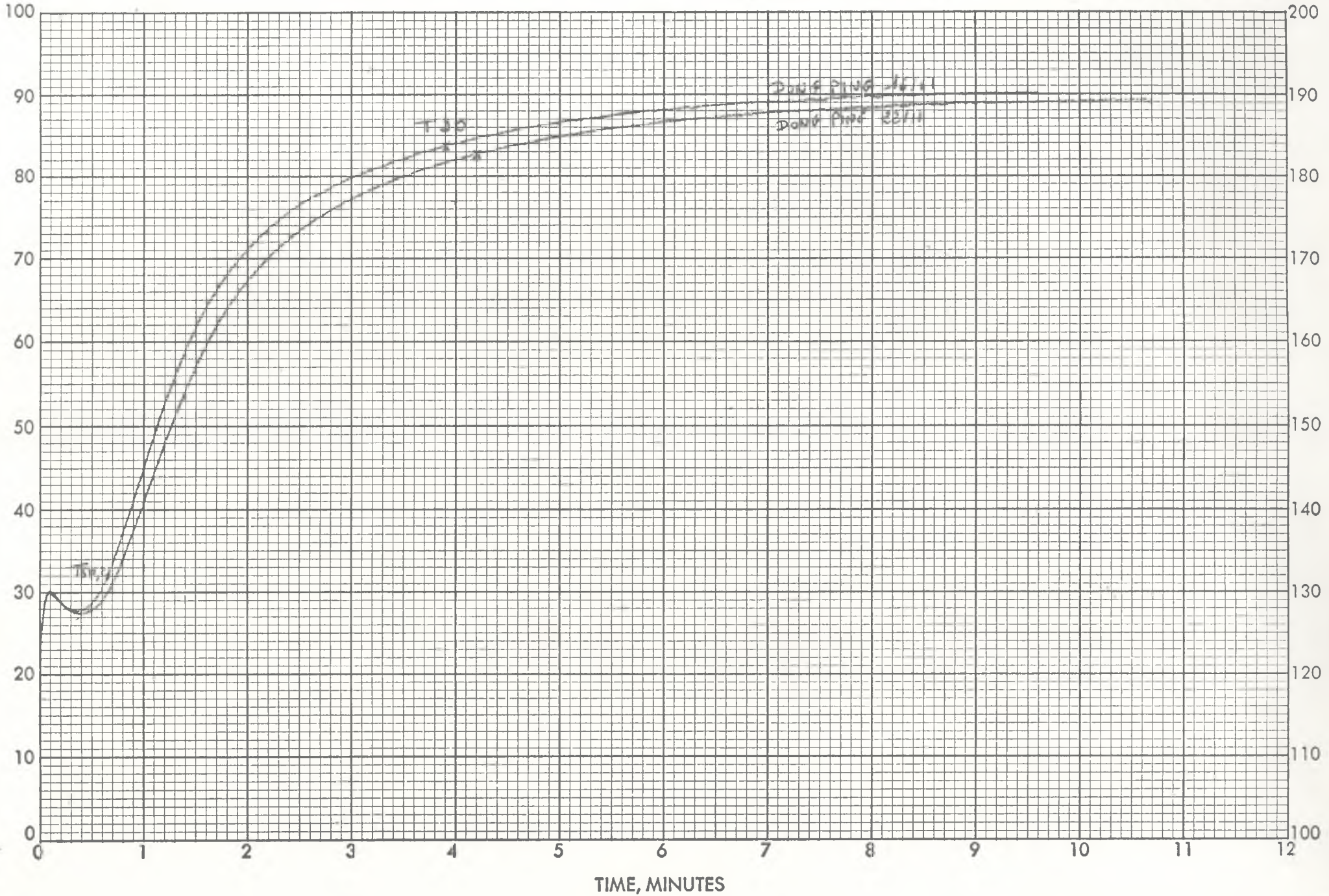
Elastic recovery curves

GRAPHIQUE RHEOMETRE

No 28163

RANGE SEL.: 50 ARC ±: 3 ° OPER.: Renault

PREHEAT: sec. TEMP.: 160 °C PROJ. NO.: Caoutchoucs Chimiques °C

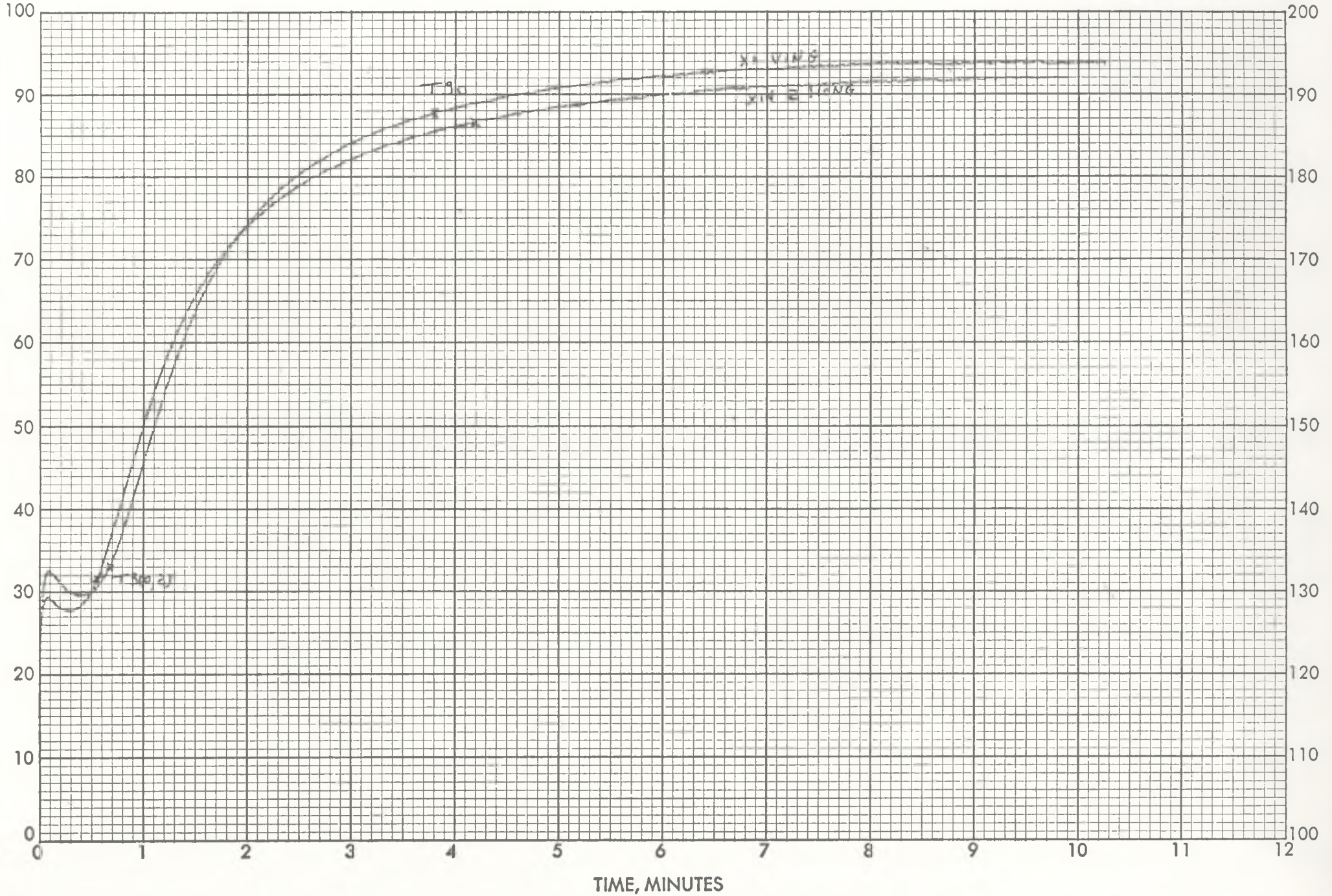


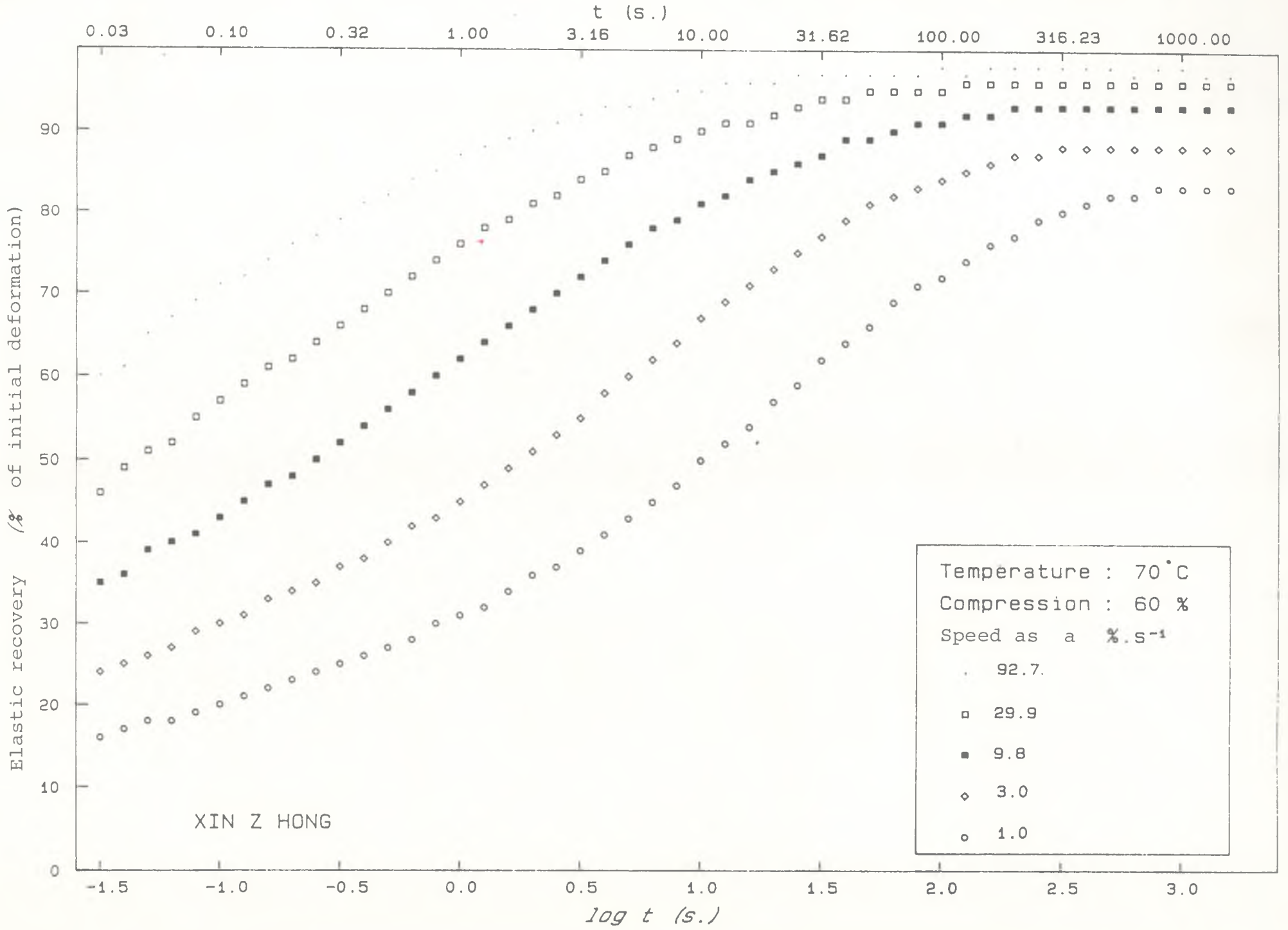
GRAPHIQUE RHEOMETRE

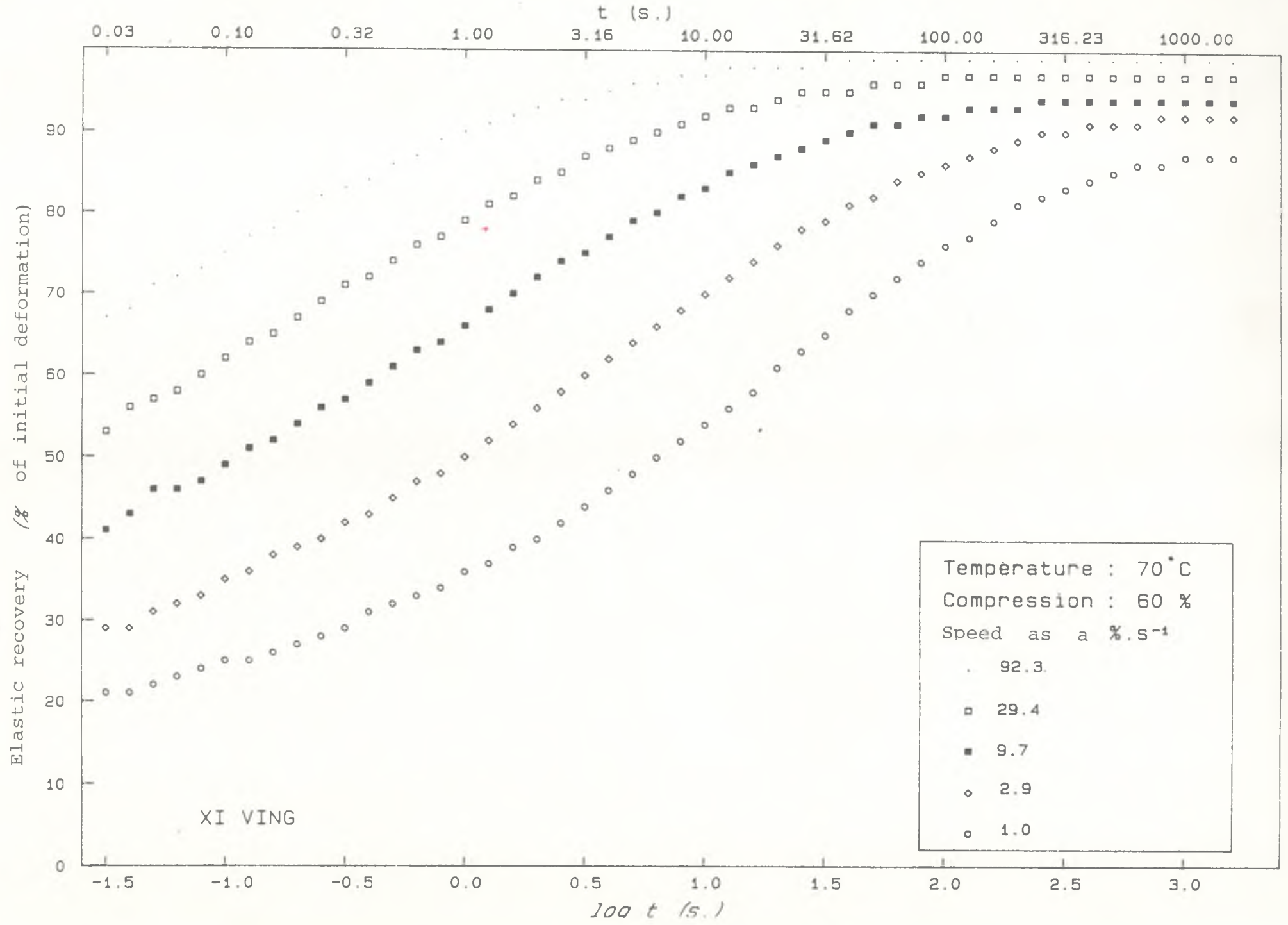
No 28163

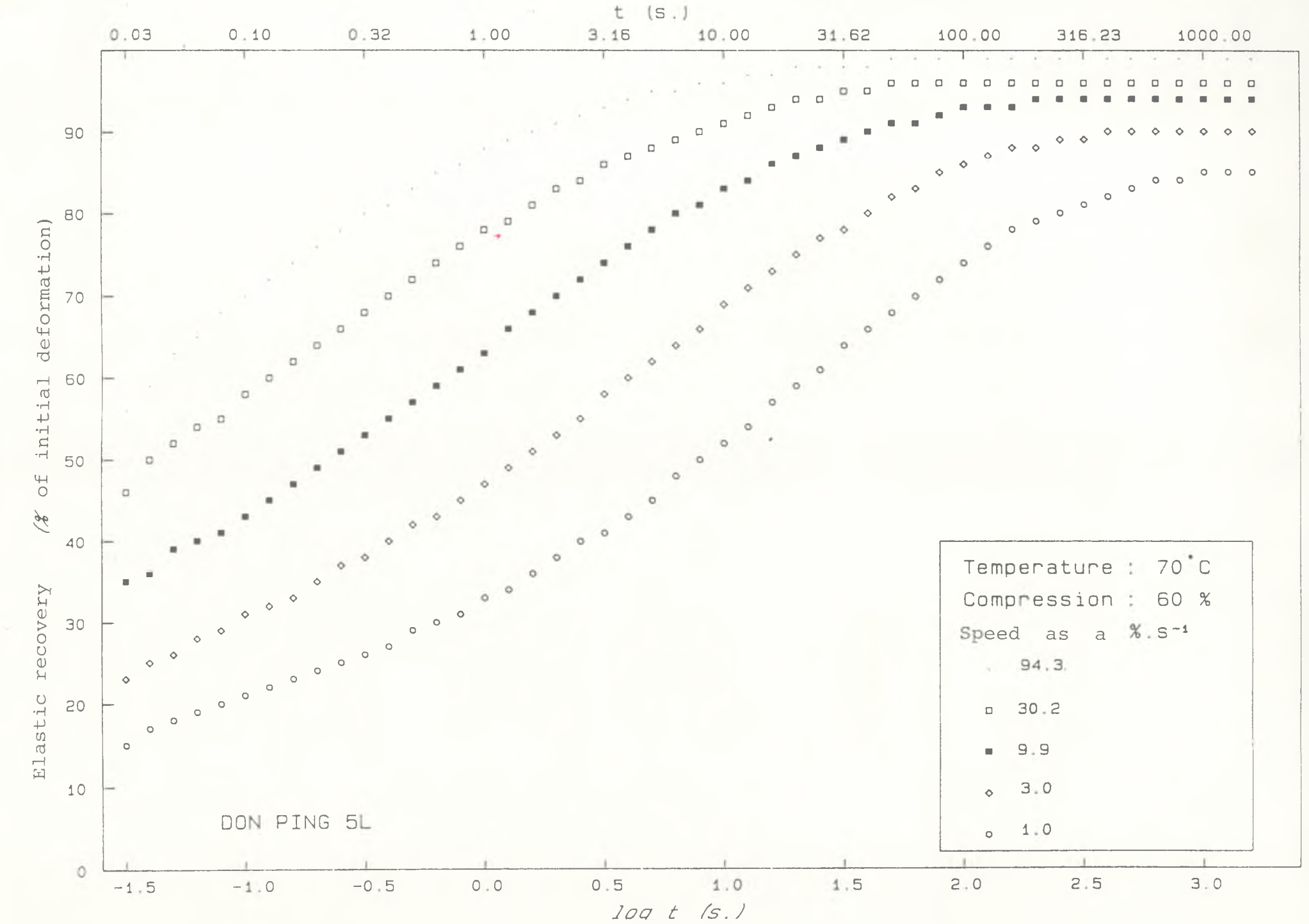
RANGE SEL.: 50 ARC ±: 3 ° OPER.: ROUSULT

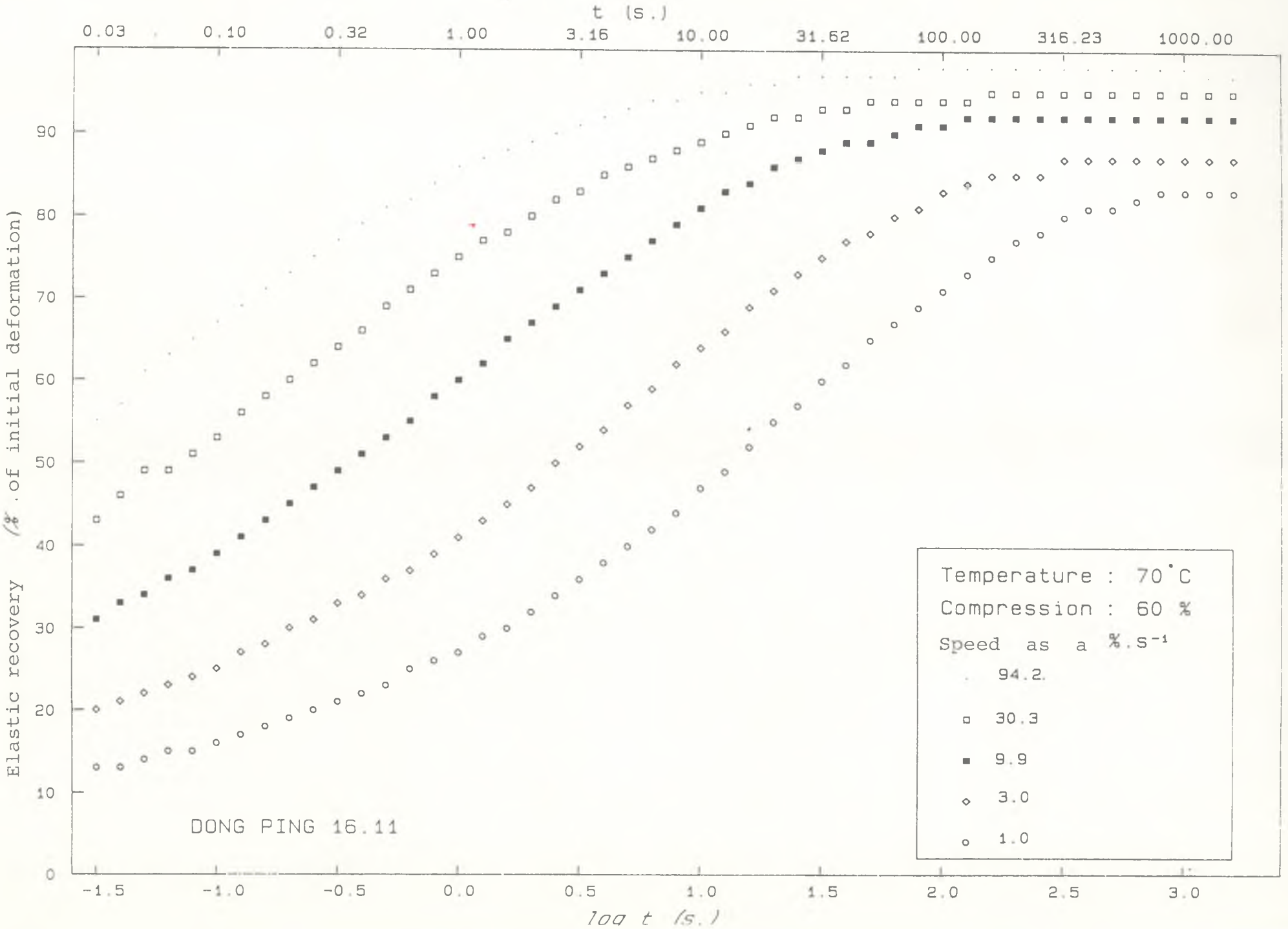
PREHEAT: sec. TEMP.: 160 °C PROJ. NO.: Caoutchoucs Chimiques °C




t (s.)
0.03
0.10
0.32
1.00
3.16
10.00
31.62
100.00
316.23
1000.00
Elastic recovery (% of initial deformation)
0
10
20
30
40
50
60
70
80
90
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
log t (s.)
XIN Z HONG
Temperature : 70°C
Compression : 60 %
Speed as a %.s-1
92.7
29.9
9.8
3.0
1.0


t (s.)
0.03
0.10
0.32
1.00
3.16
10.00
31.62
100.00
316.23
1000.00
Elastic recovery (% of initial deformation)
0
10
20
30
40
50
60
70
80
90
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
log t (s.)
XI VING
Temperature : 70°C
Compression : 60 %
Speed as a %.s-1
92.3
29.4
9.7
2.9
1.0


t (s.)
0.03
0.10
0.32
1.00
3.16
10.00
31.62
100.00
316.23
1000.00
Elastic recovery (% of initial deformation)
0
10
20
30
40
50
60
70
80
90
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
log t (s.)
DON PING 5L
Temperature : 70°C
Compression : 60 %
Speed as a %.s⁻¹
94.3
30.2
9.9
3.0
1.0


t (s.)
0.03
0.10
0.32
1.00
3.16
10.00
31.62
100.00
316.23
1000.00
Elastic recovery (% of initial deformation)
0
10
20
30
40
50
60
70
80
90
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
log t (s.)
DONG PING 16.11
Temperature : 70°C
Compression : 60 %
Speed as a %.s-1
94.2
30.3
9.9
3.0
1.0